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Electron ionization mass spectra of monosaccharide *O*-methyloxime trifluoroacetates

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ABSTRACT

Electron ionization mass spectra for trifluoroacetate (TFA) derivatives of aldose, ketose, and deoxyaldose *O*-methyloximes are reported. Typical fragmentation patterns include loss of F, CH_3O, CF_3CO, or CF_3CO_2 fragments from the generally observable parent ion, as well as cleavage between each of the sugar C–C chain bonds. The most intense ions result from loss of trifluoroacetic acid and/or trifluoroacetic anhydride from these primary fragments. Suitable high-mass and fragmentation ions are present to make this technique a useful structural probe. During the preparation of fructose TFA *O*-alkyloximes, partial conversion to 1-chloro-1-deoxyfructose derivatives is observed due to displacement of an *O*-trifluoroacetyl group by chloride ions present in the reaction mixture.

INTRODUCTION

Carbohydrate trifluoroacetate (TFA) derivatives have been shown to have very favorable properties with respect to both gas–liquid chromatography (g.l.c.)[1–3] and mass spectroscopic (m.s.)[4–6] analyses. While chemical ionization (c.i.) mass spectra are much more likely to show parent ions (usually M + 1) than electron ionization (e.i.) mass spectra, electron ionization mass spectra exhibit more fragment ions and hence generally provide more structural information than most c.i. mass spectra. It is therefore surprising that only c.i.-m.s. data have been reported for sugar *O*-alkyloxime TFA derivatives[7,8]. We report herein e.i. mass spectra for these derivatives and show how these spectra can in fact provide useful structural information. We also report an unusual side-reaction observed in the preparation of ketose *O*-substituted oxime trifluoroacetates.

RESULTS

Monosaccharide *O*-benzyloxime trifluoroacetates are extraordinarily well-resolved by g.l.c. on DB-1701 capillary columns (cyanopropylphenyl silicon stationary phase)[1]. Unfortunately their e.i. mass spectra are totally dominated by a peak at m/z = 91 (presumably the highly stable tropylium cation derived from cleavage and rear-

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TABLE I

Mass-spectral data for penta-*O*-acetyl-D-glucose *O*-methyloximes[a]

Ion	m/z	*I (s)*	*I (a)*	*Ion*	m/z	*I (s)*	*I (a)*
6P 5	689	0.05	—	4Cx4	505	0.19	0.17
6P 4	575	1.04	0.88	4Cx2	277	1.14	1.54
6P 1a	251	0.81	0.80	4Cx1a	181	6.76	5.38
6P 0a	137	3.09	2.38	4Cx0a	67	11.96	7.19
6F 5	670	0.37	—	4Cf3	436	0.25	0.16
6F 4	556	0.34	—	4Cf2	322	3.51	2.59
6F 3	442	0.90	—	4Cf0a	112	12.90	8.02
6Mo4	544	0.15	0.11	3Cx3	379	0.20	0.10
6Mo3	430	1.56	1.57	3Cx2	265	5.65	5.04
6Mo2	316	3.91	3.78	3Cx0a	55	26.79	13.85
6Mo2a	334	25.27[b]	22.41[b]	3Cx1′	153	22.79	19.75
6Mo1a	220	2.95	2.66				
6Mo0a	106	4.19	5.45	3Cf2	310	1.48	1.25
				3Cf1	196	10.93	12.19
6Ac3	478	0.34	0.26	3Cf0a	100	3.88	1.94
6Ac2	364	0.82	0.81				
6Ac1	250	5.00	4.91	2Cx2	253	3.10	3.02
6Ac0a	154	5.22	4.56	2Cx1	139	8.01	6.20
				2Cx0a	43	62.50	24.77
6Ao4	576	2.30	0.17				
6Ao3	462	2.22	0.98	2Cf1	184	50.36	46.65
6Ao2	348	10.69	4.39	2Cf0	70	3.41	5.15
6Ao1	234	3.39	7.64	2Cf1′	185	100.00	100.00
6Ao2a	366	0.16	0.11	2Cf0′	88	25.98	12.60
6Ao1a	252	0.91	0.94				
6Ao0a	138	7.30	3.95	1Cx1	127	7.37	5.86
5Cx5	631	0.04		1Cf0	58	38.44	26.05
5Cx2	289	0.92	0.74	1Cf0′	59	26.92[c]	14.62[c]
5Cx1a	193	8.60	11.52				
5Cx0a	79	3.49	2.08	Cyclic	207	0.80	10.14
5Cf4	562	0.08	—	CF_3Est	129	21.03	18.70
5Cf2	334	25.27	22.41	$AllCF_3$	109	32.59	24.08
5Cf1	220	2.95	2.66	CF_3COH_2	99	23.93	15.55
5Cf0	106	4.19	5.45	CF_3CO	97	69.55	44.82
5Cf0a	124	3.39	2.39	C_5H_5O	81	20.56	14.12
				F_2CCO	78	18.44	10.89
				CF_3	69	satd.	satd.

[a] See the first footnote in the text and elsewhere in the text for ion-assignment abbreviations: I (s) = relative intensity of *syn*-oxime ions [I (m/z = 185) = 100.00 = 35 840 ion counts, — = less than 10 ion counts, satd. = saturated], I (a) = relative intensity of *anti*-oxime ions [I (m/z = 185) = 100.00 = 12 192 ion counts]. [b] Most of the intensity is probably due to 5Cf2 ion at same mass. [c] Some of the intensity may be due to $[CH_3OCO]^+$.

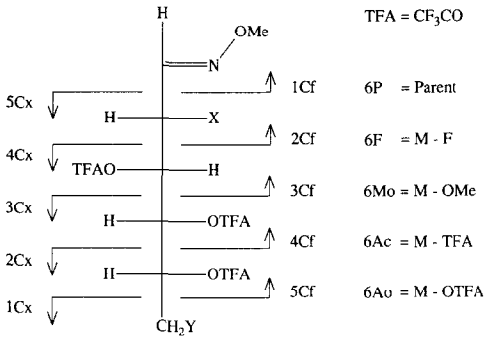


Fig. 1. Mass-spectral fragmentation pathways of the per-*O*-(trifluoroacetyl) aldose *O*-methyloximes: (*i*) of D-glucose, X = Y = OTFA; (*ii*) of 2-deoxy-D-*arabino*-hexose, X = H, Y = OTFA; (*iii*) of D-rhamnose, X = OTFA; Y = H (*syn*-isomers shown).

rangement of the benzyl group from the sugar oxime). The corresponding *O*-alkyloxime trifluoroacetates are slightly less well-resolved by g.l.c.[1,2], but their e.i. mass spectra are much more informative.

Table I gives the primary observed ions for both the *syn* and *anti* isomers of penta-*O*-acetyl-D-glucose *O*-methyloxime, together with their assignments* (see Figure 1). Particularly notable are the presence of a weak but observable parent ion (6P5) and easily detected $[M - CF_3CO_2]^+$ (6Ao4) and $[M - CF_3CO_2H]^{+\cdot}$ (6P4) ions. Structurally diagnostic ions resulting from fragmentation of each of the aldose C–C chain bonds are also present (nCxm and nCfm). These fragments then undergo repeated loss of trifluoroacetic acid and/or trifluoroacetic anhydride, often to give very intense ions. These findings parallel those reported for alditol TFA derivatives by Chizhov *et al.*[4], except that the alditols do not exhibit a $[M - CF_3CO_2H]^{+\cdot}$ peak. Ions associated with the loss of F, CF_3CO, and CH_3O groups are also present in varying amounts. The first two of these fragmentation patterns were not noted in the previous study of alditol trifluoroacetates[4], but these patterns have been reported in the spectra of non-oximated aldose and ketose TFA derivatives[5,6] and observed in spectra of alditol trifluoroacetates collected on our spectrometer. Spectral data for the *O*-methyloxime TFA derivatives of representative 2- and 6-deoxyhexoses, a hexulose, and a hexitol are given in Tables II–V, respectively. A summary of the contributions observed for the different fragmentation pathways is given in Table VI.

* Fragment-ion identifications are abbreviated as nXm where n = the number of sugar-derived carbon atoms in the fragment ion, m = the number of intact CF_3 groups in the fragment ion, and X identifies the primary fragment lost (P = none, *e.g.*, parent ion, F = –F, Mo = $-CH_3O$, Mf = $-CF_3$, Ac = $-CF_3CO$, Ao = $-CF_3CO_2$, Cx = chain fragmentation starting at the oxime end [for aldoses, loss of the $-CH-NOCH_3$ oxime group (58 daltons)], Cf = chain fragmentation starting at the other end (typically, loss of the terminal $-CH_2O_2CCF_3$ group (127 daltons, with a prime mark (′) used to denote cleavage with hydrogen-atom transfer. The loss of trifluoroacetic acid molecules (114 daltons from a primary ion is therefore indicated by a series of ions with decreasing m-values. If a molecule of trifluoroacetic anhydride (210 daltons) is also lost, an "a" is appended to the fragment identifier, i.e., nXma. Unk = other significant ions whose assignment is unknown. Other abbreviations are either obvious or given elsewhere in the text.

TABLE II

Mass-spectral data for 2-deoxy-tetrakis-*O*-(trifluoroacetyl)-D-*arabino*-hexose-*O*-methyloximes[a]

Ion	m/z	*I (s)*	*I (a)*	*Ion*	m/z	*I (s)*	*I (a)*
6P 4	577	0.21	0.18	4Cf2	324	0.27	0.21
6P 3	463	7.50	9.43	4Cf1	210	16.17	18.36
6P 2	349	3.95	5.02	4Cf0	96	15.55	15.55
6P 1	235	4.43	5.05	4Cf0a	114	1.56	1.68
6P 1a	253	2.10	2.34				
6P 0a	139	6.36	7.00	3Cx3	379	0.17	0.15
				3Cx2	265	1.03	1.44
6F 3	558	0.44	—	3Cx0a	55	49.72	47.90
6F 2	444	0.61	0.16	3Cx1′	153	16.24	19.28
6F 1	330	1.54	0.25				
				3Cf1	198	14.16	16.20
6Mo3	432	0.20	0.31	3Cf0	84	4.34	19.46
6Mo2	318	0.97	1.53				
6Mo1	204	6.81	12.85	2Cx2	253	2.10	2.34
6Mo0	90	5.83	9.74	2Cx1	139	6.36	7.00
6Mo2a	336	1.60	2.05	2Cx0a	43	100.00	100.00
6Mo1a	222	80.55[b]	98.63[b]				
6Mo0a	108	11.12[b]	13.29[b]	2Cf0	72	21.62	16.07
				2Cf0′	73	42.83	45.17
6Ac3	480	0.15	0.23				
6Ac2	366	8.15	9.44	1Cx1	127	5.35	7.05
6Ac1	252	1.90	2.46	1Cf0	58	21.31	35.14
6Ac0	138	10.81	12.13	1Cf0′	59	33.34[c]	36.08[c]
				Unk	209	—	9.69
6Ao3	464	3.44	2.54	Cyclic	207	4.52	3.45
6Ao2	350	8.78	9.24	Unk	205	4.87	4.38
6Ao1	236	26.97	17.33	Unk	179	6.17	6.96
6Ao0	122	12.98	19.62	Unk	176	6.09	8.56
6Ao0a	140	3.16	3.59	Unk	125	6.41	8.34
				Unk	112	8.08	8.48
5Cx4	519	0.13	—	Unk	110	13.28	14.00
5Cx1	177	4.32	5.32				
5Cx0	63	2.13	2.42	CF_3COH_2	99	16.52	21.17
5Cx0a	81	23.45	31.51	CF_3CO	97	43.03	48.90
				Unk	82	26.14	25.76
5Cf2	336	1.60	2.05	CF_3	69	satd.	satd.
5Cf1	222	80.55	98.63	Unk	54	39.72	33.40
5Cf0	108	11.12	13.29	CH_3COH_2	45	49.86	55.15
				CH_3CNH	42	44.55	32.67
4Cx4	505	0.05	0.04	CH_3CN	41	39.72	40.86
4Cx2	277	0.34	0.68				
4Cx1	163	1.14	1.03				
4Cx1a	181	10.83	11.00				
4Cx0a	67	12.14	13.05				

[a] See the first footnote in the text and elsewhere in the text for ion-assignment abbreviations: I (s) = relative intensity of *syn*-oxime ions [I (m/z = 43) = 100.00 = 46 400 ion counts, — = less than 10 ion counts, satd. = saturated], I (a) = relative intensity of *anti*-oxime ions [I (m/z − 43) − 100.00 = 30 464 ion counts]. [b] Most of the intensity is probably due to 5Cf1/5Cf0 ions at the same mass. [c] Some of the intensity may be due to CH_3OCO.

TABLE III

Mass-spectral data for tetrakis-*O*-(trifluoroacetyl)-L-rhamnose *O*-methyloximes[a]

Ion	m/z	*I (s)*	*I (a)*	*Ion*	m/z	*I (s)*	*I (a)*
6P 4	577	0.47	0.52	4Cf3	436	0.42	0.48
6P 3	463	1.66	2.26	4Cf2	322	6.45	8.88
6P 2	349	0.36	1.89	4Cf1	208	0.95	1.62
6P 1	235	6.01	8.02	4Cf0	94	3.03	4.38
6P 0a	139	7.49	8.23	4Cf0a	112	14.73	16.81
6F 3	558	1.69	—	4Cx3	393	0.62	1.06
6F 2	444	0.38	0.11	4Cx2	279	4.27	6.10
6F 1	330	1.14	0.41	4Cx1	165	9.36	12.65
6F 0a	234	1.15	1.52	4Cx0	51	11.78	14.21
				4Cx1a	183	0.62	4.62
6Mo4	546	0.08	0.16				
6Mo3	432	0.62	0.86	3Cf2	310	1.65	2.34
6Mo2	318	3.79	6.23	3Cf1	196	6.69	9.74
6Mo1	204	7.80	13.52	3Cf0	82	8.15	7.35
6Mo1a	222	3.22	3.12	3Cf0a	100	3.36	3.12
6Mo0a	108	6.20	7.30				
				3Cx2	267	0.54	0.59
6Ac3	480	0.04	—	3Cx1	153	7.14	7.53
6Ac2	366	0.91	1.23	3Cx0a	57	50.46	61.05
6Ac1	252	2.33	3.26				
6Ac0	138	3.12	3.11	2Cf1	184	37.85	43.11
6Ac0a	156	3.73	5.04	2Cf0	70	—	8.65
				2Cf1′	185	57.05	76.46
6Ao3	464	7.11	1.28	2Cf0′	88	18.56	17.62
6Ao2	350	10.54	11.02				
6Ao1	236	32.90	29.68	2Cx1	141	78.06	99.09
6Ao0	122	2.86	10.97				
				1Cf0	58	44.59	64.82
5Cf4	562	0.06	—	1Cf0′	59	26.36[b]	30.07[b]
5Cf3	448	0.07	—				
5Cf2	334	29.30	39.66	Unk	390	0.72	1.03
5Cf0a	124	4.87	4.67	Unk	265	2.18	2.83
				Unk	209	0.70	5.36
5Cx4	519	0.12	0.07	TFAVCO	167	16.56	24.28
5Cx3	405	0.05	0.09	CF_3Est	129	18.67	27.37
5Cx2	291	0.87	1.14	Unk	113	29.87	52.67
5Cx1	177	2.17	2.97	$AllCF_3$	109	28.53	39.92
5Cx1a	195	2.10	4.02	CF_3CO	97	53.24	61.77
5Cx0a	81	25.57	36.80	CF_3	69	satd.	satd.
				Unk	53	41.40	50.06
				Unk	47	58.39	56.63
				CH_3CO	43	85.79	91.55
				C_3H_5	41	100.00	100.00

[a] See the first footnote in the text and elsewhere in the text for ion-assignment abbreviations: I (s) = relative intensity of *syn*-oxime ions [I (m/z = 41) = 100.00 = 62 144 ion counts, — = less than 10 ion counts, satd. = saturated], I (a) = relative intensity of *anti*-oxime ions [I (m/z = 41) = 100.00 = 24 608 ion counts]. [b] Some of the intensity may be due to CH_3OCO.

TABLE IV

Mass-spectral data for pentakis-*O*-(trifluoroacetyl)-D-fructose *O*-methyloximes[a]

Ion	m/z	*I (A)*	*I (B)*	*Ion*	m/z	*I (A)*	*I (B)*
6P 5	689	—	0.05	3Cx3	379	0.55	0.34
6P 4	575	1.30	1.03	3Cx2	265	15.23	9.98
6P 1a	251	2.50	1.43	3Cx1	151	2.41	1.26
6P 0a	137	11.89	6.48	3Cx1a	169	5.95	3.76
				3Cx0a	55	26.93	23.85
6F 4	670	0.50	—	3Cx1′	153	22.32	12.70
6F 2	442	1.45	0.11				
6F 0a	232	1.04	0.46	3Cf2	310	1.12	—
				3Cf0a	100	48.36	38.84
6Mo4	544	—	0.18	3Cf2′	311	27.46	18.24
6Mo2	316	15.95	10.38				
6Mo2a	334	7.05[b]	3.84[b]	2Cx2	253	3.11	1.43
6Mo1a	220	11.68[b]	4.46[b]	2Cx1	139	12.25	7.35
6Mo0a	106	4.50	2.66	2Cx0a	43	41.14	47.63
6Ac3	478	0.52	0.40	2Cf1	184	3.25	2.51
6Ac2	364	4.27	2.74				
6Ac1	250	2.50	2.97	1Cx1	127	27.43	32.92
6Ac0a	154	10.00	5.41				
				1Cf0	127	27.43	32.92
6Ao4	576	2.45	0.60				
6Ao3	462	3.59	2.31	Unk	318	2.79	4.75
6Ao2	348	47.50	25.09	Unk	288	3.48	2.14
6Ao1	234	6.12	2.93	Unk	222	7.77	7.08
6Ao0a	138	62.79	41.08	Unk	197	5.61	5.40
				Unk	196	5.07	4.71
5Cx4	562	—	0.04	Unk	192	7.05	2.93
5Cx3	448	0.68	0.30	Unk	183	7.84	10.33
5Cx2	334	7.05[b]	3.84[b]	TFAVCO	167	10.29	9.35
5Cx1	220	11.68[b]	4.46[b]	Unk	166	9.34	5.16
5Cx0a	124	5.89	3.44	Unk	164	9.16	5.77
				Unk	155	9.50	5.53
5Cf4	562	—	0.04	CF_3Est	129	8.12	7.70
5Cf3	448	0.68	0.30	Unk	110	12.00	7.54
5Cf2	334	7.05[b]	3.84[b]	$AllCF_3$	109	12.57	10.05
5Cf0a	124	5.89[b]	3.44[b]	CF_3COH_2	99	57.07	86.16
				CF_3CO	97	74.14	66.71
4Cx3	391	—	0.09	C_3H_5O	81	14.39	12.81
4Cx2	277	2.21	1.45	F_2CCO	78	16.37	14.09
4Cx1a	181	5.45	4.16	CF_3	69	satd.	satd.
4Cx0a	67	10.91	9.45	CH_3OCO	59	22.68	24.03
				CH_3COH_2	45	100.00	100.00
4Cf2	322	2.91	1.92				
4Cf1a	226	1.37	0.49				
4Cf0a	112	4.30	2.92				

[a] See the first footnote in the text and elsewhere in the text for ion-assignment abbreviations: I (s) = relative intensity of *syn*-oxime ions [I (m/z = 45) = 100.00 = 5600 ion counts, — = less than 10 ion counts, satd. = saturated], I (a) = relative intensity of *anti*-oxime ions [I (m/z = 45) = 100.00 = 25664 ion counts]. [b] 6Moma, 5Cxm, 5Cf, 5Cxma, and 5Cfma ions have masses in common.

TABLE V

Mass-spectral data for hexakis-*O*-(trifluoroacetyl)-D-glucitol[a]

Ion	m/z	*I*	*Ion*	m/z	*I*
6P 4	530	0.08	5Cf5	631	1.22
6P 3	416	0.58	5Cf4	517	0.06
6P 2	302	2.07	5Cf3	403	0.14
			5Cf2	289	0.69
6F 6	739	0.23	5Cf1a	193	14.14
6F 5	625	0.03			
6F 4	511	0.08	4Cf4	505	2.38
6F 3	397	0.15	4Cf3	391	0.70
6F 1	169	4.89	4Cf2	277	2.00
6F 2a	301	1.31	4Cf1a	181	7.55
6Mf3	461	0.02	3Cf3	379	5.13
6Mf2	347	0.28	3Cf2	265	14.32
6Mf1	233	0.87	3Cf1	151	1.45
6Mf0a	137	1.87	3Cf1a	169	4.89
			3Cf0a	55	32.94
6Ac3	433	0.01	3Cf1′	153	17.38
6Ac2	319	0.35			
6Ac1	205	0.74	2Cf2	253	27.20
6Ac0	91	0.93	2Cf1	139	11.25
6Ac0a	109	2.44	2Cf0a	43	100.00
6Ao5	645	1.88	1Cf1	127	15.09
6Ao4	531	0.60			
6Ao3	417	0.56	Unk	473	0.05
6Ao2	303	8.24	Unk	404	0.18
6Ao1	189	1.72	Unk	237	3.15
6Ao1a	207	27.38	Unk	221	2.45
6Ao0a	93	31.59	Unk	165	4.33
			Unk	125	5.61
			$TFAOH_2$	115	4.07
			CF_cOH_2	99	27.80
			CF_3CO	97	58.50
			F_2CCO	78	14.49
			CF_3	69	satd.
			Unk	65	33.79
			CH_3OCO	59	16.54
			CF_2	50	10.82
			C_3H_5	41	11.96

[a] See the first footnote in the text and elsewhere in the text for ion-assignment abbreviations: I = relative intensity of ions [I (m/z = 43) = 100.00 = 136960 ion counts, — = less than 10 ion counts, satd. = saturated].

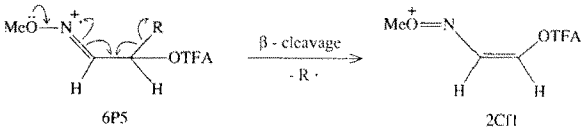
TABLE VI

Summary of mass-spectral fragmentation pathways

	Percent contributions of different ion series[a]								
Ion	D-*Glucose*		*2-DG*		D-*Rhamnose*		D-*Fructose*		D-*Glucitol*
Series	*s*	*a*	*s*	*a*	*s*	*a*	*s*	*a*	
6P	0.9	1.0	4.0	4.0	2.7	3.1	3.2	2.5	0.9
6F	0.4	0.0	0.5	0.0	0.7	0.3	0.4	0.3	2.0
6Mo	2.8	3.6	3.2	2.9	4.0	4.5	7.8	5.9	—
6Ac	2.0	2.6	3.4	3.5	1.8	1.7	3.4	3.9	1.4
6Ao	4.8	4.3	8.8	7.7	7.9	7.3	24.6	20.2	20.7
5Cx	2.4	3.6	4.8	5.6	5.6	6.5	5.2	3.4	4.6
5Cf	6.5	7.6	15.1	16.5	6.1	6.5	2.8	2.2	—
4Cx	3.7	3.3	3.9	3.8	4.9	4.2	3.6	4.2	3.7
4Cf	3.1	2.6	5.3	5.2	4.7	4.7	1.6	1.4	—
3Cx	6.1	4.5	8.2	7.1	10.5	8.6	10.2	11.0	17.0
3Cx′	4.4	4.8	2.6	2.7	—	—	4.4	3.7	4.9
3Cf	3.0	3.6	2.9	5.2	3.6	3.2	10.0	11.0	—
3Cf′	—	—	—	—	—	—	5.4	5.1	—
2Cx	13.7	8.1	17.3	15.8	14.4	14.4	11.2	16.0	39.7
2Cf	9.8	12.4	3.5	2.3	6.9	7.6	0.6	0.8	—
2Cf′	23.3	26.9	6.9	6.5	13.7	13.7	—	—	—
1Cx	1.3	1.4	0.8	1.0	—	—	5.4	9.3	4.3
1Cf	7.0	6.2	3.4	5.1	8.1	9.4	5.4	9.3	—
1Cf′	5.0	3.6	5.3	5.2	4.7	4.4	—	—	—

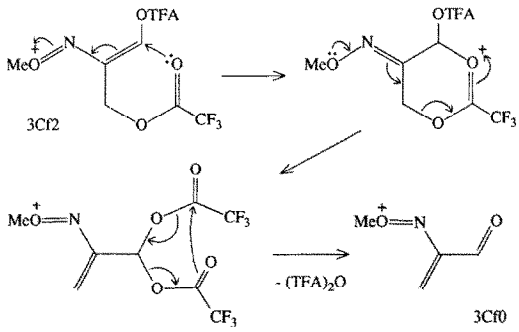
[a]Percentages based on tabulated fragmentation patterns only: 2-DG = 2-deoxy-D-*arabino*-hexose, s = *syn*-oxime, a = *anti*-oxime.

An examination of the data reveals a number of features. The oxime group exhibits the directing effects expected for a carbonyl-type functionality[9]: (a) α-cleavage (aldose 1Cf1 and ketose 5Cx ions, the ketose 2Cf ion is surprising small) and (b) β-cleavage with γ-hydrogen rearrangement (aldose 2Cf1′ and ketose 3Cf′ ions, the former undergoing subsequent loss of $CF_3CO\cdot$ to give 2Cf0′). The presence of two adjacent heteroatoms in the oxime appears to also facilitate a β-cleavage without hydrogen-atom migration (aldose 2Cf ions, Eq. 1), a reaction not normally seen in other carbonyl-like compounds. In the corresponding ketose 3Cf2 fragmentation, facile loss of trifluoroacetic anhydride follows to give the 3Cf0a ion, again aided by the second heteroatom (Eq. 2).



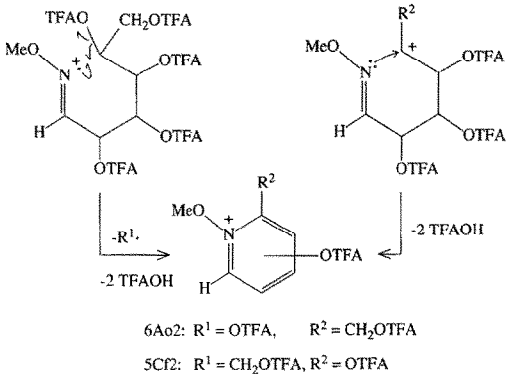
6P5 2Cf1 (1)

Another highly characteristic set of reactions derived from the oxime functionality gives rise to what are probably quaternary pyridinium ions (D-glucose, 6Ao2 and



(2)

5Cf2; 2-deoxy-D-*arabino*-hexose, 6Ao1 and 5Cf1; L-rhamnose, 6Ao1 and 5Cf2, and D-fructose, 6Ao2). These would arise from trapping of δ-carbonium ions by the nucleophilic oxime nitrogen and/or by S_H2 displacement (rearrangement displacement[9]) at the δ-carbon by an oxime cation radical (illustrated for glucose in Eq. 3), followed in both cases by loss of two moles of trifluoroacetic acid to achieve aromatization.

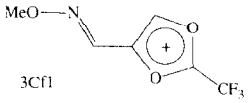


(3)

The *syn* and *anti* oxime isomers exhibit several very characteristic differences. In particular, the *syn*-isomers give rise to high-mass nFm and nAom ions that are as much as five to ten times as intense as the corresponding ions in the *anti*-isomers. Differences between hydroxyl group isomers were less pronounced*.

Other structurally significant ions arise from fragmentations directed by the trifluoroacetate groups, leading to loss of the oxime functionality. The resulting nCxm ions are identical to the per-*O*-(trifluoroacetyl) alditol nCfm ions for which explanations have already been published[4]. We would simply note the possibilities for stabilization by delocalization (e.g., 3Cf1) and the apparent tendency of the smaller 4Cx, 3Cx and 2Cx

* A brief analysis was conducted for the four pentoses, D-arabinose, D-lyxose, D-ribose, and D-xylose. Relative intensity differences of a factor of 2–4 were observed in about a dozen ions, mostly those at high mass (See note at the end of the Experimental Section). It may be difficult, however, to obtain meaningful stereochemical information from these data. For example, there was no obvious correlation with the expected ease of formation of the proposed cyclic pyridinium ions.

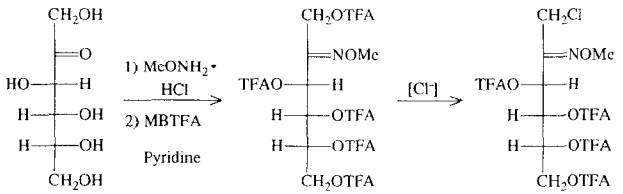


ions to undergo loss of trifluoroacetic anhydride with hydrogen-atom migrations to give the acylium ions $[H_2C{=}C{=}CHCO]^+$ (4Cx0a), $[H_2C{=}CHCO]^+$ (3Cx0a), and $[CH_3CO]^+$ (2Cx0a), respectively. Another ubiquitous trifluoroacetate-derived ion is $[H_2C{=}CHCH{=}OCOCF_3]^+$ (3Cx1′), m/z = 153).

It is not clear whether the 6Mo2 and 6Mo1 ions (or their much more intense pentose 5Mo2 and 5Mo1 counterparts) are the result of loss of $CH_3O\cdot$ and CF_3CO_2H or from the loss of $CF_3CO_2\cdot$ and CH_3OH. Another ambiguity concerns the ion at m/z = 59. This could be an α-cleavage ion with hydrogen-atom migration (1Cf0′, $[H_2C{=}NOMe]^{+\cdot}$) and/or a trifluoroacetate-derived ion such as $[CH_3OCO]^+$. (The same ion is present in the mass spectrum of hexakis-*O*-(trifluoroacetyl)-D-glucitol, but it is only about half as intense as it is in the oxime trifluoroacetates).

The lower mass portions of the spectra contain a number of other intense ions. Typical of most perfluoro compounds, the largest peak in all of the spectra is the CF_3 ion. Other strong ions and their possible assignments are: m/z = 97 ($[CF_3CO]^+$), m/z = 115 ($[CF_3C(OH)_2]^+$), m/z = 99 ($[CF_3C(=OH)H]^+$), m/z = 78 ($[F_2C{=}C{=}O]^{+\cdot}$), m/z = 50 ($[CF_2]^{+\cdot}$), m/z = 45 ($[CH_3(C{=}OH)H]^+$), m/z = 43 ($[CH_3CO]^+$ and/or $[HCNO]^{+\cdot}$), m/z = 42 ($[H_2C{=}C{=}O]^{+\cdot}$ and/or $[CH_3CNH]^+$), m/z = 41 ($[C_3H_5]^+$ and/or $[CH_3CN]^{+\cdot}$), m/z = 167 ($[CF_3CO_2CH{=}CH{-}CO]^+$), m/z = 109 ($[C_3H_4CF_3]^+$?), m/z = 129 ($[CF_3C(=O)OCH_3]^+$?). Cyclic structures have been proposed for the ions at m/z = 81 ($[C_5H_5O]^+$) and m/z = 207[4].

Our previous g.l.c. studies of ketose *O*-benzyloxime TFA derivatives revealed anomalous behavior, *i.e.*, the presence of more than the expected two peaks (*syn* and *anti*) per sugar, whose relative intensities varied with derivatization time[1]. The present m.s. study of the trifluoroacetylation of D-fructose *O*-methyloxime shows that the extra peaks are due to side reactions that occur during derivatization. Four g.l.c. peaks are observed, two of which can be readily identified as the expected per-*O*-TFA aldose *O*-methyloximes (Table IV). The other two peaks exhibit an apparent parent ion at m/z = 611, and isotope and fragmentation patterns consistent with their formulation as the *syn*- and *anti*-isomers of 1-chloro-1-deoxy-tetrakis-*O*-(trifluoroacetyl)-D-fructose *O*-methyloxime! These chloro derivatives result from the displacement of a trifluoroacetate by the chloride ions present in solution from the *O*-methylhydroxylamine hydrochloride (Eq. 4). Chloride substitution at the C-1 primary carbon of ketoses is consistent



(4)

with the fact that this position is both activated (by the adjacent C=N linkage) and the least sterically hindered*.

The presence of significant high-mass ions in all of the trifluoroacetate derivatives reported here, together with fragments due to cleavage of each of the sugar C–C chain bonds, make structural assignments relatively simple and reliable. While the stereochemistry of the hydroxyl substituents cannot be readily determined, the location of the carbonyl group and that of any deoxy and/or substituted carbons are generally unambiguous. This technique might therefore be developed into a useful variation of the traditional polysaccharide structural analysis scheme (g.l.c.–m.s. of partially methylated alditol acetates[10]) in which the methylated polysaccharide is hydrolyzed, and the resulting monosaccharides are directly derivatized as their per-*O*-(trifluoroacetyl) *O*-alkyloximes for analysis by g.l.c.–m.s. In addition, the high volatility of the trifluoroacetate derivatives and the previous observation of a parent ion for lactose trifluoroacetate[5], suggest that per-*O*-(trifluoroacetyl) disaccharide *O*-methyloximes might be directly analyzable on instruments capable of reaching ca. 1200 daltons.

EXPERIMENTAL

General procedure. — Trifluoroacetate derivatives were prepared[1] by treating a sugar solution [50 μL, containing a sugar (5–7 mg) in pyridine (200 μL)] with the oximation reagent [50 μL, made up of *O*-methylhydroxylamine hydrochloride (85 mg) in pyridine (4 mL)] for 30 min at 75°, followed by treatment of the cooled solution of sugar oxime with *N*-methylbis(trifluoroacetamide) (MBTFA, 10 μL) for 2 h at room temperature. Mass spectra were acquired on a Finnigan MAT 5100 quadrupole g.l.c.–m.s. instrument equipped with a J & W Scientific DB-1701 capillary column (30 m × 0.25 mm i.d., 0.25-μm film) using the following instrumental conditions: injector = 250°, column = 130° for 0.1 min, 10°.min^{-1} to 180°, 180° for 15 min (Better g.l.c. resolution can be obtained if needed by using a lower oven-temperature program.), interface = 270°, manifold = 80°, ionizing voltage = 70 eV, scan range = 40–740 daltons, scan time = 0.4 s, sampling interval = 0.1 ms, calibration gas = perfluorotributylamine. The data reported represent the sum of the five largest m.s. scans for each g.l.c. peak. Intensities are given relative to the second largest ions, since the largest ion, $m/z = 69$ (CF_3), was invariably saturated. No correction was made for background ion counts since they were observed to be negligible†.

* The only aldose that exhibits extra peaks in the g.l.c. of its *O*-TFA *O*-benzyloxime is glycolaldehyde, which also contains a primary hydroxyl group adjacent to the carbonyl group.

† Mass sprectal data for the per-*O*-TFA aldose *O*-methyloximes of D-arabinose, D-ribose, D-xylose, D-mannose, and 1-chloro-1-deoxy-D-fructose are available from the authors upon request. Data for the trifluoroacetates of 1-deoxy-D-erythritol and several 1-deoxypentitols are reported elsewhere (see ref. 11).

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